



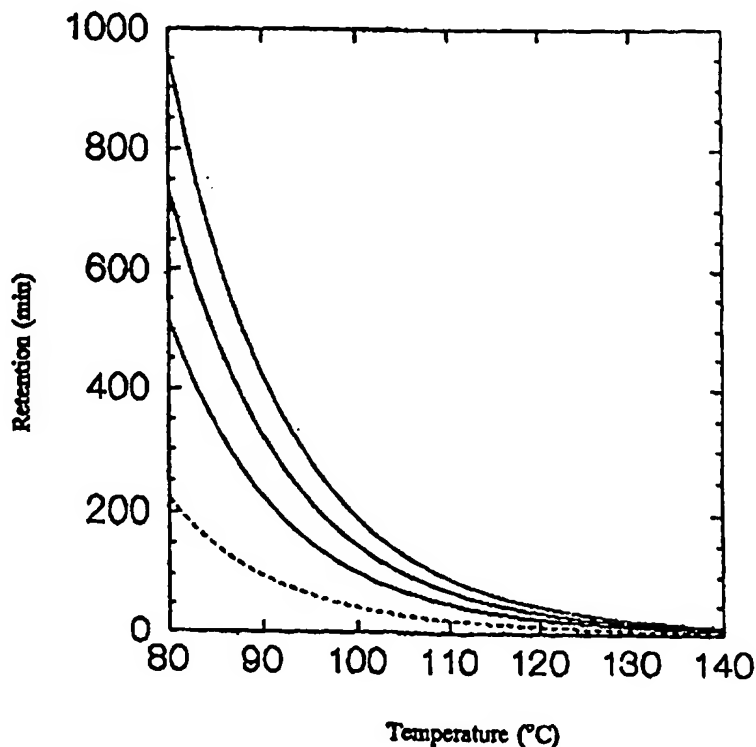
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(54) Title: METHOD FOR REMOVAL OF HEXENURONIC ACID GROUPS IN CELLULOSE PULP BY HEAT TREATMENT

(57) Abstract

Pulp, in particular hardwood pulps, is delignified in cooking and, when needed, further delignified with oxygen to a kappa number below (24), preferably below (14). The delignified pulp is heated and treated at a temperature of about 85 to 150 °C, preferably 90 to 110 °C, at a pH of about 2 to 5 in order to decrease the kappa number by 2 to 9 units by removing at least 50 % of the hexenuronic acid groups in the pulp. The treated pulp is bleached in at least one bleaching stage.



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METHOD FOR REMOVAL OF HEXENURONIC ACID GROUPS IN CELLULOSE
PULP BY HEAT TREATMENT

The present invention relates to a method of treating cellulose pulps according to claim 1.

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Pulp mills have recently attempted to abandon the use of elementary chlorine, and partly also chlorine dioxide, the reasons for this being both aspects of environmental protection and market factors. Disadvantages caused by elementary chlorine include both noticeable malodorous gaseous emissions and liquid effluents from chemical pulp mills into watersystems. Affecting primarily watersystems, chlorine dioxide does not cause odour disadvantages on such a large scale. When comparing these chlorine chemicals with each other by means of the AOX number designating the loading on watersystems, it can be noted that elementary chlorine is many times more detrimental than chlorine dioxide.

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During the past few years, a great number of chlorine-free bleaching methods have been developed in addition to those using chlorine and chlorine dioxide. For example oxygen, ozone and peroxide are used in these methods. However, in many countries sequences using chlorine dioxide are also popular, these being possible as regards to environmental aspects as well. The reasons for the popularity are manifold. The price of chlorine dioxide is very competitive compared with that of other chemicals, being today approximately half of the price of competing peroxide, for instance. Also the strength and brightness values achieved by dioxide bleaching are good, in fact at least approximately of the same scale as when using peroxide at the same consumption of chemical (kg/adt).

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When bleaching of cellulose pulps is based on such bleaching chemicals as oxygen, peroxide or ozone, removal of heavy metals forms an essential process stage. Detrimental metals

include manganese, copper and iron, which catalyze reactions harmful to the quality of pulp. They degrade bleaching chemicals, which decreases the efficiency of bleaching and increases the consumption of chemicals. In cellulose pulps, heavy metals are primarily bound to carboxyl acid groups.

It has been suggested that removal of metals be effected in such a way that prior to the critical bleaching stage, pulp is pre-treated with an acid, e.g. sulphuric acid. The published FI patent application 76134 (CA 1206704) discloses that the acid treatment is carried out at a temperature of at least 50 °C, preferably at 60 to 80 °C, at pH 1 to 5. It is stated in the publication that even acid treatment at a lower temperature results in significant removal of detrimental metal ions, but acid treatment at the temperatures according to the publication modifies lignin so that dissolution thereof is significantly improved in alkaline peroxide treatment following the acid treatment (Lachenal, D. et al., Tappi Proceedings, International Pulp Bleaching Conference, 1982, p. 145 - 151). Thus, the acid stage causes the kappa number to drop in the peroxide stage, whereas no decrease in the kappa number has been found in the acid stage. In the publication FI 76134 it is also stated that in theory, the acid treatment could be effected even at a temperature of 100 °C, but this could result in pulp of poorer quality.

In the EP patent application 511695 it is suggested that after the acid treatment, metal ions advantageous for peroxide bleaching, such as magnesium ions, should be added, since also part of these metals is removed in the acid treatment. According to this publication, the acid treatment is effected at a temperature of 10 to 95 °C, most preferably at 40 to 80 °C, and at pH 1 to 6, most preferably 2 to 4. The acid treatment is followed by a stage in which suitable alkaline earth metal is added. Further, it is mentioned that in the acid treatment, pulp can be treated with a suitable

bleaching and/or delignification chemical, such as chlorine dioxide.

5 Removal of detrimental metals may be made more efficient by using chelating agents for binding metals in connection with the acid treatment. One such method is disclosed in the SE patent 501651, which brings forward an acid treatment similar to that in the above-mentioned EP publication 511695, with the difference of the acid treatment being
10 effected in the presence of a chelating agent. However, chelating agents used for binding metals contribute to rising the bleaching costs.

15 The primary aim of the above-described acid treatments of pulp is to achieve such a composition of metals which is preferable for chlorine-free bleaching chemicals. In these stages, the kappa number may be decreased by 1 to 2 units due to a washing and extraction phenomenon. As mentioned earlier, the metal composition affects the consumption of
20 bleaching chemicals, the reason for the use of known acid stages being therefore removal of metals from the pulp.

One of the most important disadvantages of prior art bleaching is still rather a great consumption of bleaching
25 chemicals, especially chlorine-free ones, which significantly rises the production costs of bleached pulp. Also chlorine dioxide bleaching has to be subjected to attempts to reduce the consumption of the chemical both for financial and environmental reasons. Further, a degree - in
30 some cases a great degree - of brightness reversion is a typical feature of pulps bleached with oxygen and peroxide.

An object of this invention is to eliminate or minimize the disadvantages of prior art and to achieve a totally new
35 arrangement for bleaching cellulose pulps, in particular cellulose pulps manufactured under alkaline conditions, by means of either totally chlorine-free bleaching chemicals,

or chlorine dioxide, which is still significant in pulp bleaching. Further, an object of the invention is to produce cellulose pulp easily bleached, e.g. by means of oxygen and/or peroxide.

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It is known that cellulose pulps contain 4-O-methyl- α -D-glucuronic acid groups (glucuronic acid groups). According to our recent discovery, sulphate pulps contain in addition to glucuronic acid groups also a significant amount of 4-deoxy- β -L-threo-hex-4-enopyranosyl uronic acid groups (hexenuronic acid groups) bound to xylan. The amount of these groups is in some pulps even substantially greater than the amount of known glucuronic acid groups.

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It has been discovered that in bleaching of pulp, hexenuronic acid groups consume bleaching chemicals reacting electrophilically, such as chlorine, chlorine dioxide, ozone and peracids (Buchert et al., 3rd European Workshop on Lignocellulosics and Pulp, Stockholm, 28.-31.8.1994). However, the hexenuronic acid groups do not affect the consumption of oxygen and hydrogen peroxide used as bleaching chemicals in alkaline conditions, because they do not react with said chemicals. Thus, no degradation of hexenuronic groups occurs in oxygen and/or peroxide bleaching. Instead, special problems as regards to pulps bleached with oxygen and/or peroxide are relatively low brightness, and/or a tendency of such pulps to undergo brightness reversion.

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On the basis of what was described above, our invention is based on the idea that by selectively removing hexenuronic acid groups from cellulose pulps in connection with bleaching it is possible to reduce the consumption of bleaching chemicals. Surprisingly, it has been discovered that at the same time, the brightness reversion tendency of pulp decreases. Also, bleaching becomes more selective, since the heavy metals can be removed more efficiently.

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Characteristics of the invention become apparent in the appended claims.

5 Said selective removal of hexenuronic acid groups according to the invention is effected by adjusting the water suspensions of cellulose pulps slightly acidic - typically, the pH is set between about 2 and about 5 - and by treating the water suspensions at a raised temperature. To achieve a
10 preferable result the temperature is at least 85°C, most preferably at least 90 °C. Utilization of temperatures as high as this has previously been avoided in acid treatment, because it has been assumed that the quality of pulp would suffer. The primary purpose of acid treatment has been
15 removal of detrimental metals. In above-described acid treatments, the purpose of which is removal of metals, the temperature does not play a significant role. What is significant is that the pH of the pulp is so low that metals separate from fibers. In laboratories the treatment is
20 generally carried out at room temperature. In mills removal of metals is typically effected at a temperature scale of 60 to 85 °C, which is the temperature prevailing naturally in the acid treatment stage due to water circulations. If a mill wished to practise acid treatment at a higher
25 temperature for some reason, the acid treatment stage would have to be separately heated with steam or the like manner. This has naturally been avoided since it has been assumed that the strenght qualities of the pulp would deteriorate. Therefore, according to what has been known so far, there
30 has been no reason to use hot, over 85 °C-acid stages. Higher temperatures mentioned in prior art (e.g. FI 76134) only mean that removal of metals is also possible at higher temperatures.

35 Duration of the treatment does not play a significant role in view of removal of metals, except insofar as it is sufficiently long, typically over 10 minutes. Extra time is

not harmful for removal of metals but it naturally causes extra costs to the mill, since long treatment time requires use of larger tanks. Large tanks have been avoided also because it has been feared that the acid stage would harm the strength qualities of the pulp. Thus, long treatment times in connection with acid stages as mentioned in prior art only mean that a long treatment time does not have a harmful effect on removal of metals.

In particular, it has to be noted that there have been definite reasons for avoidance of long and hot (e.g. 2 to 3 hours and 85 °C) acid treatments in mill conditions. These above-described reasons have been so significant that prior to this invention, it has not been discovered that the kappa number of pulp can be decreased by 2 to 9, preferably 3 to 6 units by means of this kind of treatment. Not even in laboratory experiments has this been discovered, since the whole idea has been regarded as being against all existing knowledge. What is especially surprising is that acid treatment like this can be carried out without damaging the strength qualities of pulp, if the kappa number of the pulp to be treated has been made to drop sufficiently, i.e. under 24, preferably under 14, by means of cooking or possibly further delignification. It has to be remembered also that pulp treatment with both acid (stage A) and chelating agents (stage Q) has been examined extremely intensively during the last five years in connection with a peroxide stage. Therefore, it is very surprising and something new to suggest a long and hot acid stage in a situation where both a high temperature and a long time, even when used separately, are regarded as detrimental factors in connection with acid treatment of pulp.

It should also be noted that pH in known acid treatments has to be rather low, i.e. 1.5-2, for decreasing e.g. the manganese content of the pulp considerably. In the pH range below 2, the carboxylic acid type groups become entirely

protonated, resulting in low metal levels. Between pH 2 and 6, metal ions compete with hydrogen ions for the carboxyl acid sites, resulting in increasing metal levels as pH increases (Devenyns, J. et al., Tappi Pulping Conference Proceedings, 1994, 381-388; Bouchard, J. et al., International Pulp Bleaching Conference 1994, 33-39). On the other hand, in the method of the present invention the carboxyl acid type groups (hexenuronic acids) are removed, which means that the amount of the carboxyl acid sites is decreased and the pulp can become occupied by metals to a less extent.

By means of the invention, it is possible to manufacture easily bleached cellulose pulp by means of a sulphate method or an equivalent alkaline method bringing hexenuronic acids into the pulp. It is characteristic of the pulp manufactured according to the invention that it contains a small amount of hexenuronic acids at the most and can be easily bleached without chlorine (ECF) or chlorine chemicals (TCF), or even with mere oxygen gas and/or peroxide. The consumption of bleaching chemicals can also be substantially reduced. Further, it is typical of the pulp produced in this way that, expressed as a pc-number, the brightness reversion thereof is smaller than 2.

The treatment of the pulp in a water suspension practised according to the invention in acidic circumstances at a temperature of at least 85 °C is hereafter also called "acidic pre-treatment".

According to the invention, cellulose pulp is treated in the presence of water at a temperature of at least 85 °C at a pH in the range from about 2 to about 5 (typically at a pH in the range from 2 to 5) in order to remove hexenuronic acid groups from the cellulose pulp. Especially preferably, the pH value of the water suspension of the cellulose pulp is maintained between 2.5 and 4. The lowest pH values (2.5 to

3.5) are preferable for softwood and the highest (3 to 4) for hardwood.

5 Various acids - inorganic acids, e.g. mineral acids such as sulphuric, nitric and hydrochloric acid, and organic acids such as formic and/or acetic acid - may be used to set the pH value for slush pulp. If so desired, the acids may be buffered, e.g. with the salts of the acids, such as formiates, in order to keep the pH value as even as possible during the treatment. There may be great variations in the temperature, ranging from 85 °C upwards. Preferably, the temperature is kept at about 90 to 110 °C. If the treatment is practised under atmospheric conditions, 100 °C is a natural maximum limit. Even higher temperatures are possible if pressure vessels are used. Thus, the treatment may be effected in a bleaching tank under pressure of 200 to 500 kPa, at a temperature of 110 to 130 °C. To avoid the excessive degradation of fiber, the maximum limit of the temperature is usually set to about 180 °C.

20 The duration of the treatment varies according to the pH value, the temperature, and the material being brought to the treatment. Naturally, it also depends on how complete a removal of hexenuronic acids is wished to be achieved. In general, the treatment time is at least t minutes, where $t = 0.5 \exp(10517/(T+273)-24)$ ($t = 0.5 e^{(10517/(T+273)-24)}$). T (°C) is the temperature of the acid treatment. The degradation of hexenuronic acid groups is in accordance with the first-order reaction kinetics. It is known that the relation between reaction rate constant k and temperature T (K) is $k = A e^{-E/RT}$ (Arrhenius Relationship), where A is the constant depending on the reaction in question, E is the activation energy and R is the gas constant. On the other hand it is known that for the first-order reaction the reaction time is $t = (1/k) \ln(c_0/c)$, where c is the concentration of the hexenuronic acids and c_0 is the original concentration. By using the Arrhenius equation and $t = (1/k) \ln(c_0/c)$ and test

results (e.g. Example 8 below) the equation of $t = 0.5 \exp(10517/(T+273)-24)$ was obtained. In general t is between 5 minutes and 10 hours. In the examples described below, the treatment is practised under atmospheric conditions. The typical treatment time at a temperature of 90 °C is about 1.5 to 6 hours, at 95 °C about 50 minutes to 5 hours, at 100 °C about 0.5 to 4 hours. Under pressure, e.g. at a temperature of 120 to 130 °C, the treatment may be effected typically within about 5 to 50 minutes.

The intention is to remove as large a part of the hexenuronic acids as possible, preferably at least about 50 %, especially preferably at least about 75 %, and most suitably at least about 90 %. The concept "pulp contains a small amount of hexenuronic acids at the most" means that the amount of hexenuronic acids is 50 % at the most, especially preferably 25 % at the most, and most suitably 10 % at the most of the amount which is present after cooking in corresponding pulp which has not been treated.

To prevent excessive degradation of carbohydrate substance, no attempts are usually made to remove the hexenuronic acid groups completely.

The treatment may be effected as continuous treatment in a flow-through reactor, or as batch treatment. Pulp is treated in the presence of water, in other words the pulp received from the pulp cooking process is slushed into water so that the consistency of the slush in the pre-treatment according to the invention is about 0.1 to 50 %, preferably about 1 - 20 %. The pre-treatment is preferably effected subject to the mixing. In continuous mixing, stationary mixers may be used.

The arrangement according to the invention may be applied to pulps which are produced by means of a sulphate process or other alkaline methods and contain hexenuronic acid groups.

The term "sulphate process" means a cooking method, the primary cooking chemicals of which are sodium sulfide and sodium hydroxide. Other alkaline cooking processes include for example extended cooks based on extending conventional sulphate cooking until the kappa number of the pulp has dropped below the value of approximately 20. These methods typically comprise oxygen treatment. Extended cooking methods include for example extended batch cooking (+AQ), EMCC (extended modified continuous cook), batch cooking, Super-Batch/O₂, MCC/O₂ and continuous cooking/O₂. According to our experiments, hexenuronic acids form about 0.1 to 10 mol-% of the hydrolysis products of the xylanase treatment of softwood pulp received from said cooking methods. After the pre-treatment according to the invention the concentration of hexenuronic acids will drop to about 0.01 to 1 mol-%.

In this application, the term "in connection with bleaching" means that the acidic pre-treatment is effected either prior to bleaching, during bleaching or, at the latest, after bleaching. When substances reacting electrophilically, e.g. chlorine, chlorine dioxide, ozone or peracids, are used as bleaching chemicals, it is especially preferable to effect the pre-treatment prior to bleaching because in this way it is possible to reduce the consumption of bleaching chemicals. It can also be stated that the treatment is practised to unbleached pulp in order to change characteristics. e.g. bleachability, of cellulose pulp. On the other hand, when using oxygen gas and/or peroxide in bleaching (or bleaching treatment), it is also possible to effect the pre-treatment after bleaching. In the latter case, the treatment is preferably carried out immediately after bleaching prior to possible drying of the pulp (i.e. to never-dried pulp). The pre-treatment may be effected between the bleaching stages of a bleaching sequence.

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The following may be mentioned as examples of suitable bleaching sequences:

- A-O-Z-P
 AQ-O-Z-P
 A-O-ZQ-P
 A-O-P_n
 5 AQ-O-P_n
 O-A-Z-P
 O-AQ-Z-P
 O-A-ZQ-P
 O-A-P_n
 10 O-AQ-P_n
 O-A-D-E-D
 O-AD-E-D
 A-O-D-E-D
 O-A-X-P_n
 15 A = acidic pre-treatment at a raised temperature according
 to the invention
 O = oxygen treatment
 P = peroxide treatment
 P_n = several subsequent peroxide treatment stages
 20 E = alkali stage
 Z = ozone treatment (ZQ meaning that complexing agent is
 added in ozone treatment)
 Q = complexing agent treatment (AQ meaning that complexing
 agent is added in acid treatment)
 25 D = chlorine dioxide treatment (AD meaning that there is no
 washing between the stages)
 X = enzyme treatment

30 Between bleaching stages using an oxygen chemical, there may
 be alkali stages. In order to make bleaching more efficient,
 known enzymes, such as cellulases, hemicellulases and
 lignases may be used.

35 The pre-treatment according to the invention is effected in
 a bleaching sequence either prior to an oxygen or peroxide
 stage, or subsequent to that, but prior to a chlorine
 dioxide stage, ozone stage or peracid stage (e.g. a formic

acid or peracetic acid stage), in order to reduce the consumption of ozone and/or peracids. Since it is possible to improve bleachability of pulps by means of the pre-treatment, the invention enables the consumption of said
5 bleaching chemicals to be decisively reduced, and/or the use of chlorine dioxide, ozone or peracids in bleaching to be eliminated.

Many chemical methods of producing chemical pulp have as the
10 last stage an oxygen delignification stage. The treatment may be effected either prior to this oxygen stage, or subsequent to it, preferably subsequent to the oxygen stage. In bleaching of hardwood pulp, the consumption of chlorine dioxide has decreased by 30 - 40 % at a brightness level ISO
15 88 %, the bleaching sequence being O-A-D-E-D. In bleaching softwood pulp, the corresponding reduction of consumption has been 10 - 20 %. In both cases the yield has remained almost unchanged compared with bleaching without stage A. Additionally, experiments have shown that stage D following
20 stage A may be carried out without washing between the stages, in other words the sequence is hereby O-AD-E-D.

In chlorine-free bleaching sequences comprising a bleaching stage with an electrophilic bleaching chemical, e.g. ozone
25 or peracid, it is preferable that the acid treatment is carried out prior to the first stage Z, and preferably in such a way that the pulp is washed before moving on to stage Z, in order to guarantee efficient removal of hexenuronic acids from the pulp. The ozone consumption caused by
30 hexenuronic acids (HexA) and thereby also the saving in the chemical consumption achieved by means of the method according to the invention can be calculated theoretically by taking into account that the hexenuronic acid consumes an equivalent amount of ozone (1 eq O_3 /HexA). Typically, the
35 saving in the consumption is 1 to 3 kg O_3 per ton pulp. In the acid treatment, furan derivatives forming out of hexenuronic acids consume twice the amount of ozone, and

therefore it is preferable to wash the pulp as efficiently as possible after the acid treatment, prior to the bleaching stage. Everything above concerns also all other chlorine-free electrophilic bleaching chemicals, such as peracetic acid, persulphuric acid and peroxomolybdates.

Reducing the consumption of the bleaching chemical by means of the acid treatment is based on the fact that in removal of hexenuronic acids, the amount of reactive acid groups in bleaching is decreased, and thus there will also be less material to be bleached.

According to one preferable embodiment, the primary bleaching chemical used is peroxide-containing substance (usually hydrogen peroxide). Thus, it is possible to produce pulp, the brightness reversion tendency of which, expressed as a pc-number, is smaller than 2. The brightness reversion tendency cannot be prevented by any other efficient way than by removing hexenuronic acids. Since in the acid treatment according to the invention also detrimental heavy metal concentrations may be reduced, it is preferable to effect the acid treatment prior to the first P-stage. Peroxide treatment is most suitably accompanied by oxygen gas pre-treatment.

The pH of the slushed pulp treated with oxygen is first set to the value of about 3 - 4 and the temperature of the pulp is raised to 90 - 130 °C, at which temperature it is kept at least 5 minutes, subsequent to which it is treated with hydrogen peroxide under alkaline conditions in order to produce bleached pulp. Instead of hydrogen peroxide, a peroxide-containing substance may be for example Caro's acid or a corresponding substance, which degrades in suitable conditions (e.g. alkaline conditions) forming hydrogen peroxide or peroxo-ions.

In order to remove heavy metals bound to the cellulose pulp, the pre-treatment according to the invention may be effected in the presence of chelates which bind heavy metals. EDTA and DTPA may be mentioned as examples of these chelating agents. In general, chelating agents are dosed into the pulp in the proportion of about 0,2 % of the pulp. It can be mentioned, though, that one special advantage of the acidic pre-treatment according to the invention is that metals can be removed rather efficiently even without chelating agent treatment, as is disclosed in Example 10.

The acidic pre-treatment may also be practised to unbleached or bleached pulp to modify characteristics relating to the qualities of paper. Thus, by removing acid groups water retention capacity of the pulp can be decreased, whereby it is possible to produce stiffer pulp applicable for use in packing boards, for example.

The invention and embodiments thereof are described in detail below by way of examples.

Fig. 1 graphically illustrates the effect of acidity on the hydrolysis velocities of arabinose acid groups and hexenuronic acid groups of pine sulphate pulp at a temperature of 80 °C. Theoretical curves have been fitted to experimental points in accordance with the equations illustrated in Example 2 respectively.

Fig. 2 illustrates the dependency of the time needed for removal of hexenuronic acid groups on the temperature at a scale of 80 to 140 °C, birch sulphate pulp having been treated with acid at pH 3.5. At this pH the reaction velocity is nearly maximal. At higher pH values the retention time shall be longer at a certain temperature. The three upper curves illustrate the optimal operating range, wherein 95, 90 and 80 % of the hexenuronic acid groups have been removed. The broken line illustrates the lowest limit

of the retention time, where 50 % of the hexenuronic acid groups have been removed.

In the examples the kappa numbers of the pulps have been defined according to standard SCAN-C 1:77, the viscosity according to standard SCAN-CM 15:88, and the brightness according to standard SCAN-C 11:75. The brightness reversion tendency is measured by means of a dry heating method (24 h, 105 °C). The pc number was counted from the results.

Example 1

4-O-methylglucuronoxylan isolated from hardwood was treated in 1 M sodium hydroxide liquor at a temperature of 160 °C for 2 hours. The liquor was cooled and the xylan precipitated from the liquor by adjusting the liquor neutral. The precipitated xylan was washed and dried, subsequent to which it was treated with endoxylanase.

The hydrolysate was fractionated by using anion exchange chromatography and gel filtration. In this way, the oligosaccharide fraction was isolated, which fraction was by means of NMR spectroscopy discovered to contain 4-deoxy- β -L-threo-hex-4-enuronoxylotriose (80 %) and -tetraose (20 %).

Part of the oligosaccharide liquor was dissolved into 10 mM acetate buffer (pH 3.7) in deuterium oxide. The liquor was inserted into an NMR tube and changes therein were followed by means of ^1H NMR spectroscopy at a temperature of 80 °C for 17 hours.

The degradation of hexenuronic acid groups was in accordance with the first order. The conversion was 55 % 17 hours after the reaction time. Hydrolysis of xylosidic linkages was not to be discovered. When hexenuronic acid groups degraded, an almost equivalent amount of compounds was generated, which compounds were identified as furan-2-carboxylic acid ($\delta_{\text{H3}} = 7.08$ ppm), $J_{\text{H3,H4}} = 3.5$ Hz, $J_{\text{H4,H5}} = 1.7$ Hz, $J_{\text{H3,H5}} = 0.8$ Hz), and

formic acid ($\delta_{\text{H}} = 8.37$ ppm). In addition, a small amount of component identified as 2-furaldehyde-5-carboxylic acid ($\delta_{\text{H3}} = 7.13$ ppm, $\delta_{\text{H4}} = 7.52$ ppm, $\delta_{\text{CHO}} = 9.60$ ppm, $J_{\text{H3},\text{H4}} = 3.5$ Hz) was generated.

5

According to the example, the hexenurosidic linkages may be selectively hydrolyzed under mild conditions without significant hydrolysis of xylosidic linkages. Correspondingly, it can be concluded that glucosidic and
10 mannosidic linkages of cellulose and glucomannan, being stronger than xylosidic linkages of xylan, are stable in these conditions.

Example 2

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Pine sulphate pulp (kappa number 25.9) was incubated in buffered liquors (pH 1.5 - 7.8) at different temperatures (25, 50 and 80 °C) for 2 hours. Subsequent to the treatments, the pulp samples were washed with water. The
20 washed pulps were treated with xylanase, and the hydrolysates were analyzed by means of ^1H NMR spectroscopy.

Changes in the carbohydrate composition of the pulp were found only at the highest temperature used (80 °C).
25 Deviating from hydrolysis of ordinary glycosides, hydrolysis of hexenuronic acid groups was not directly proportional to the hydronium ion concentration (Equation 1), but the pH dependancy of the reaction velocity clearly showed that the reaction occurred through a free hexenuronic acid group
30 without catalysis caused by a hydronium ion (Equation 2, Fig. 1).

$$(1) \quad k = k_0 [\text{H}_3\text{O}^+]$$

$$(2) \quad k = k_0 \{1/(1 + K_a/[\text{H}_3\text{O}^+])\}$$

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According to the example, hexenuronic acid groups of the cellulose pulp may be selectively removed under slightly

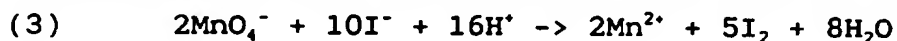
acidic conditions (pH > 2) at a raised temperature. Partial hydrolysis of arabinose groups occurs, but the loss in yield caused by this is diminutive due to the low concentration of arabinose in cellulose pulps (softwood pulps 1 %, hardwood pulps 0 %).

Example 3

The oligosaccharide liquor (15.5 mg, 0.025 mmol) was added into boiling 0,01 M formiate buffer (pH 3.3, 27ml). The liquor was refluxed for 3 hours. Samples (0.5 ml) were taken at suitable intervals and diluted with water (5 ml). The absorption of light was measured at a wavelength scale of 200 - 500 nm. Forming of furan-2-carboxylic acid ($\lambda_{\max} = 250$ nm) was in accordance with the first order ($k = 0,44 \text{ h}^{-1}$). The molar absorptivity calculated per amount of the hexenuronic acid groups was 8,700. This absorptivity value may be used to define the hexenuronic acid concentration of cellulose pulps.

Example 4

The oligosaccharide mixture (2.0 mg, 3.22 μmol) was dissolved into water (4.8 ml). 0.6 ml 2 M sulphuric acid and 0.6 ml 0.02 M potassium permanganate (12.0 μmol) was added into the liquor. In ten minutes, 0.12 ml 1 M potassium iodide and 100 ml water was added into the liquor. The iodine concentration of the liquor was defined spectrophotometrically (350 nm, $\epsilon = 16,660$). The consumption of permanganate was calculated on the basis of Equation 3.



The consumption of permanganate was 7.98 μmol , i.e. 2.5 calculated per equivalent hexenuronic acid group. Since the definition of kappa number used for representing lignin concentration of cellulose pulps is done under exactly the same reaction conditions, hexenuronic acid groups may cause

a considerable error in respect to the real lignin concentration.

Example 5

5

Birch sulphate pulp (3 g, kappa number 16.5) was treated in 0.06 M formiate buffer (pH 3.2, 250 ml) at a temperature of 100 °C for 4 hours. Degradation of hexenuronic acid groups was followed by means of absorption of light (250 nm, $\epsilon = 8,700$) caused by 2-furan-carboxylic acid. The total amount of hexenuronic acid groups was calculated to be 70 meq/kg of pulp. The kappa number of the treated pulp was 10.6.

According to the invention, a considerable amount of hexenuronic acid groups can be removed from sulphate pulp, due to which the kappa number used for representing the delignification grade drops significantly. A similar reduction can be expected to occur in the consumption of electrophilic bleaching chemicals reacting with hexenuronic acid groups.

Example 6

Pine sulphate pulp bleached with oxygen and peroxide (9 g, kappa number 5.3) was treated in 0.06 M formiate buffer (pH 3.2, 600 ml) at a temperature of 100 °C for 2.5 hours. Degradation of hexenuronic acid groups was followed by means of absorption of light (250 nm, $\epsilon = 8,700$) caused by 2-furan-carboxylic acid.

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The total amount of hexenuronic acid groups was calculated to be 48 meq/kg of pulp. All hexenuronic acid groups were removed from the pulp in the reaction time of about 30 minutes. The treated pulp was filtered in a Büchner funnel, and washed with water. Compared with the original pulp, the treated pulp was infiltrated very easily. The kappa number of the treated pulp was 2.3.

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The kappa number of sulphate pulp bleached with oxygen and peroxide according to the invention is very low after treatment removing hexenuronic acid groups. The treatment according to the invention significantly improves possibilities to produce full-bleached TCF pulps without ozone bleaching.

Example 7

Birch sulphate pulp (100 g, kappa number 11.5) bleached with oxygen was mixed in water (3 l). The pH of the suspension was adjusted to the value 3.4 by adding 2 ml strong formic acid. The suspension produced in this way was incubated at a temperature of 100 °C for 4 hours. Degradation of hexenuronic acid groups was followed by means of UV absorption (250 nm, $\epsilon = 8,700$) caused by 2-furan-carboxylic acid. The amount of the removed hexenuronic acid groups was calculated to be 54 meq/kg of pulp, which is approximately 98 % of the total amount of hexenuronic acid groups of the pulp. The kappa number of the treated pulp was 6.2.

Chelating with EDTA (0.2 % of the pulp) was carried out to both treated and non-treated pulp at a concentration of 3.5 %. The treatment was practised at a temperature of 60 °C, the duration thereof being 45 minutes.

After washing, peroxide bleaching (3 % of the pulp being hydrogen peroxide) was effected to the pulps at a concentration of 10 %. Magnesium sulphate (0.5 % of the pulp) was used as stabilizer, and sodium hydroxide (1.8 % of the pulp) as alkali, the temperature being 90 °C and the bleaching time 180 minutes. The kappa number, viscosity, brightness and brightness reversion tendency (pc number) were defined of the washed pulps. The characteristics of the pulps are shown in Table 1.

Table 1. The effect of the pre-treatment (A) on bleachability with peroxide (P) of birch sulphate pulp bleached with oxygen (O)

	Stage	Residue H ₂ O ₂ (% of pulp)	Kappa no.	Viscosity (ml/g)	Brightness (% ISO)	pc no.

	O		11.5	1165	49.7	
10	OP	0	9.3	1125	61.0	2.5
	OA		6.2	1065	49.9	
	OAP	2.1	3.2	980	76.1	1.1

15 The results show that the pre-treatment strongly affected the action of the pulp in the peroxide stage. The consumption of peroxide was crucially reduced, but in spite of that, the rise in brightness was more than twice as great compared to the non-treated pulp. The brightness reversion

20 tendency of the pre-treated pulp was, expressed as a pc number, over 50 % lower than the brightness reversion tendency of the non-treated pulp.

Example 8

25 Unbleached birch sulphate pulp (kappa number 15.4) was treated with formic acid at a concentration of 5 % so that the pH of the slush was 3.0, 3.5 or 4.0. The pulps treated in this way were incubated in 150 ml-pressure vessels at

30 temperatures of 85, 95, 105 and 115 °C for 0.2 - 24 hours. Disengagement of hexenuronic acid groups was followed by defining the concentrations of furan derivatives having formed out of hexenuronic acid groups in the filtrate.

35 The kappa number and viscosity were defined of the incubated pulps.

The decrease in the kappa number was in a linear way dependent on the decrease in the hexenuronic acid concentration. The maximal reduction of hexenuronic acid concentration was 60 meq/kg, corresponding to a 6.3-unit reduction of the kappa number. 90 % of the hexenuronic acid groups being removed, the yield of the treatment was 98 % calculated on the basis of TOC. The degradation of hexenuronic acid groups was in accordance with the first order reaction kinetics. The minimum retention time (reduction of 50 % in the hexenuronic acid concentration) required by the treatment, and the optimal retention time (reduction of 80 - 95 % in the hexenuronic acid concentration) are illustrated by means of curves fitted to experimental points (Fig. 2). At pH 3.0 - 3.5 the degradation velocity of hexenuronic acid groups was very close to its maximum value. At higher pH values the retention times required are longer due to a slower reaction velocity.

Example 9

Birch sulphate pulp (kappa number 10.3) bleached with oxygen was treated under conditions according to Example 8 to remove hexenuronic acid groups. The kappa number after the treatment was 5.4. Both acid-treated and non-treated pulp was bleached with DED sequence using several doses of chlorine dioxide and alkali. Being bleached to the brightness level 88.0 % ISO, the acid-treated pulp consumed 2.5 % chlorine dioxide calculated as active chlorine, and 1.4 % sodium hydroxide. The corresponding consumption percentages of chlorine dioxide and sodium hydroxide by the non-treated pulp were 4.3 and 0.8, respectively. The yield of the DED sequence was 97.1 % for the acid-treated pulp and 95.5 % for the non-treated pulp. Thus, removal of hexenuronic acid groups caused the consumption of chemicals of the ECF bleaching to decrease by 42 - 43 % without lowering the yield of the bleaching. The tensile index and

tear index of the sheets made of the pulps were identical at the same density of the sheet.

Example 10

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Pine sulphate pulp (100 g, kappa number 25.9) was mixed in water (3 l). The pH of the suspension was adjusted to the value 3.5 by adding 1.5 ml strong formic acid. The suspension produced in this way was incubated at a temperature of 100 °C for 2.5 hours. Degradation of hexenuronic acid groups was followed by means of UV absorption (250 nm, $\epsilon = 8,700$) caused by 2-furan-carboxyl acid. The total amount of the removed hexenuronic acid groups was calculated to be 32 meq/kg of pulp, which corresponds to about 95 % of all hexenuronic acid groups of the pulp. Chelating with EDTA (0.2 % of the pulp) was carried out to both non-treated and treated pulp at a concentration of 3 %. The treatment was effected at a temperature of 50 °C, the duration thereof being 45 minutes. The metal concentrations of the pulps were defined with an atomic absorption spectrophotometer.

The treatment removing hexenuronic acid groups decreased especially iron and manganese concentrations of the pulp (Table 2). The decrease in iron was in this case significantly greater than when using chelate treatment, and even the decrease in manganese was as great as when using chelate treatment.

Table 2. The effect of the pre-treatment (A) and chelating (Q) on metal concentrations of pine sulphate pulp (mg/kg)

35

Treatment	Iron	Copper	Manganese
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-				
		22.0	6.5	36.8
	A	10.7	5.7	2.4
5	Q	20.9	0.9	1.8
	AQ	10.4	1.3	0.2

10 Since iron and manganese are the most detrimental metals as
regards to TCF bleaching, the use of chelating agents may be
replaced either partly or totally with treatment removing
hexenuronic acids. If chelating agents are used, it is
preferable to add them in connection with the treatment
15 removing hexenuronic acid groups.

While the invention has been described in connection with
what is presently considered to be the most practical and
preferred embodiment, it is to be understood that the
20 invention is not to be limited to the disclosed embodiment,
but on the contrary, is intended to cover various
modifications and equivalent arrangements included within
the spirit and scope of the appended claims.

Claims:

- 5 1. A method of treating cellulose pulps manufactured by means of a sulphate process or the like alkaline method, characterized in that cellulose pulp is heated and treated at a temperature of about 85 to 150 °C at a pH of about 2 to 5 to remove at least about 50 % of the hexenuronic acid groups in the cellulose pulp, so that the kappa number of
10 the pulp decreases 2 - 9 units.
2. A method according to claim 1, characterized in that the treatment is effected in connection with bleaching.
- 15 3. A method according to claim 2, characterized in that the treatment is effected in a bleaching sequence prior to a chlorine dioxide stage, with the object of reducing the consumption of chlorine dioxide in bleaching.
- 20 4. A method according to claim 2, characterized in that the treatment is effected in a bleaching sequence prior to an ozone or peracid stage, with the object of reducing the consumption of ozone or peracid.
- 25 5. A method according to claim 2, characterized in that the treatment is effected in a bleaching sequence prior to an oxygen or peroxide stage, or subsequent to it, and that the bleached pulp is produced, the brightness reversion tendency of which, expressed as a pc number, is smaller than 2.
- 30 6. A method according to claim 1, characterized in that the treatment is effected at a consistency of 0.1 to 50 %.
- 35 7. A method according to claim 1, characterized in that the treatment is effected at a pH value of 2.5 to 4.

8. A method according to any of the preceding claims, characterized in that the pH of the cellulose pulp is set by means of an inorganic or organic acid.

5 9. A method according to claim 1, characterized in that the cellulose pulp is treated with oxygen prior to the treatment.

10 10. A method according to claim 1, characterized in that the temperature is about 90-110 °C.

11. A method according to claim 1, characterized in that pulp is heated with steam or the like.

AMENDED CLAIMS

received by the International Bureau on 11 March 1996 (11.03.96);
original claims 1-11 replaced by amended claims 1-11 (2pages)]

1. A method of treating cellulose pulps manufactured by means of a sulphate process or the like alkaline method, characterized in that cellulose pulp is heated and treated at a temperature of about 85 to 150 °C at a pH of about 2 to 5 to remove at least about 50 % of the hexenuronic acid groups in the cellulose pulp and to decrease the kappa number of the pulp by 2 - 9 units, and that the treated pulp is bleached.

2. A method of treating cellulose pulps manufactured by means of a sulphate process or the like alkaline method, characterized in that cellulose pulp is heated and treated at a temperature of about 85 to 150 °C at a pH of about 2 to 5 for at least a time t , where $t = 0.5 e^{10517/(T-273)-24}$, in minutes, and where T is the treatment temperature (°C), to remove at least about 50 % of the hexenuronic acid groups in the cellulose pulp and to decrease the kappa number of the pulp by 2 - 9 units, and that the treated pulp is bleached.

3. A method of treating cellulose pulps manufactured by means of a sulphate process or the like alkaline method, characterized in that cellulose pulp is heated and treated at a temperature of about 85 to 150 °C at a pH of about 2 to 5 to remove at least about 50 % of the hexenuronic acid groups in the cellulose pulp and to decrease the kappa number of the pulp by 2 - 9 units, and that the treatment is effected in a bleaching sequence prior to a chlorine dioxide stage, with the object of reducing the consumption of chlorine dioxide in bleaching.

4. A method according to claim 1 or 2, characterized in that the treatment is effected in a bleaching sequence prior to an ozone or peracid stage, with the object of reducing the consumption of ozone or peracid.

5. A method according to claim 1 or 2, **characterized** in that the treatment is effected in a bleaching sequence prior to an oxygen or peroxide stage, or subsequent to it, and that the bleached pulp is produced, the brightness reversion tendency of which, expressed as a pc number, is smaller than 2.
6. A method according to claim 1, 2 or 3, **characterized** in that the treatment is effected at a consistency of 0.1 to 50 %.
7. A method according to claim 1, 2 or 3, **characterized** in that the treatment is effected at a pH value of 2.5 to 4.
8. A method according to claim 1, 2 or 3, **characterized** in that the pH of the cellulose pulp is set by means of an inorganic or organic acid.
9. A method according to claim 1, 2 or 3, **characterized** in that the cellulose pulp is treated with oxygen prior to the treatment.
10. A method according to claim 1, 2 or 3, **characterized** in that the temperature is about 90-110 °C.
11. A method according to claim 1, 2 or 3, **characterized** in that pulp is heated with steam or the like.

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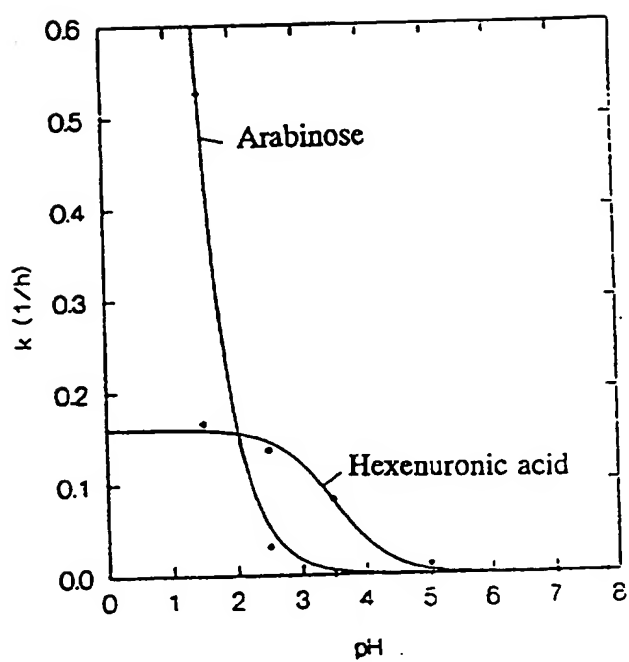


FIG. 1

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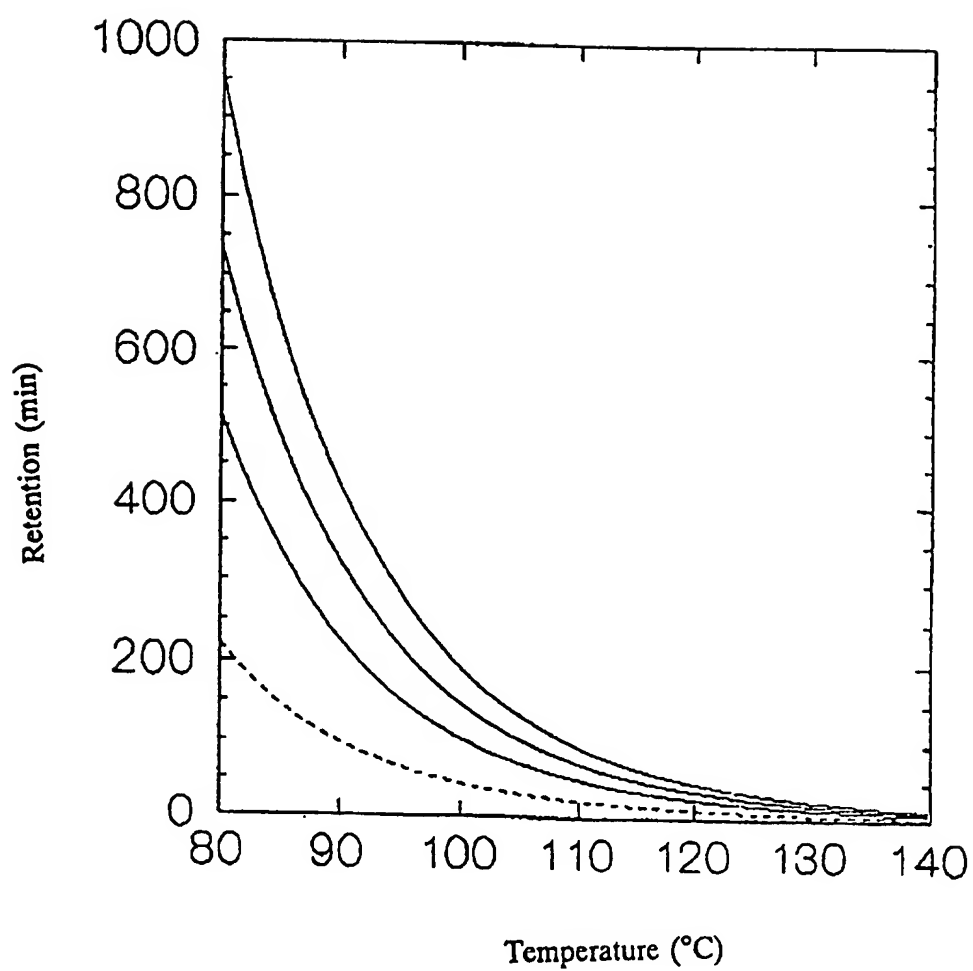


FIG.2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 95/00566

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 9/00, D21C 9/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0456626 A1 (EKA NOBEL AB), 13 November 1991 (13.11.91), page 3 - page 6, claims 1,10, abstract --	1-2,4-11
X	EP 0511695 A1 (EKA NOBEL AB), 4 November 1992 (04.11.92), page 3, line 52 - line 58, claims 1,2, 10, abstract --	1-2,4-11
A	WO 9311296 A1 (VALTION TEKILLINEN TUTKIMUSKESKUS), 10 June 1993 (10.06.93), page 1 - page 7, abstract -- -----	1-11

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

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15 -02- 1996

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INTERNATIONAL SEARCH REPORT

Information on patent family members

05/01/96

International application No.

PCT/FI 95/00566

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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EP-A1- 0511695	04/11/92	AU-B- 651192 AU-A- 1514992 CA-A- 2067296 CA-A- 2139246 EP-A- 0679760 JP-A- 5148784 NZ-A- 242465 SE-B- 470065 SE-A- 9101301	14/07/94 11/03/93 31/10/92 31/10/92 02/11/95 15/06/93 23/12/93 01/11/93 31/10/92
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